

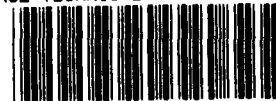
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<p>The susceptibilities for second harmonic generation (SHG) $\chi_{31}^{(2)}$ and $\chi_{33}^{(2)}$ of a new high T_g polymer, 1,2-benzyl-1,2-cyclohexyl-bridged syndioregic α-cyanocinnamicamide (BCSCCA) have been measured by using a Maker fringe apparatus. The BCSCCA was spin coated on a quartz substrate. The film of about 1 μm thickness has shown a large birefringence before poling, thus indicating molecular alignment due to spin coating. The polar order was induced by poling the film at 215°C with the corona discharge. The SHG coefficients d_{33} is equal to 3.54 pm/V and $d_{13} = 0.95$ pm/V at 532 nm. The d-coefficients are stable and show negligible decay over one month. The SHG intensities at 532, 528, 476, 403, 366 nm are also observed. A large resonance enhancement in the SHG intensity was observed inside the absorption band.</p>			
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Electro-Optics and Second Harmonic Generation of Nonlinear Optical Polymers

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ABSTRACT

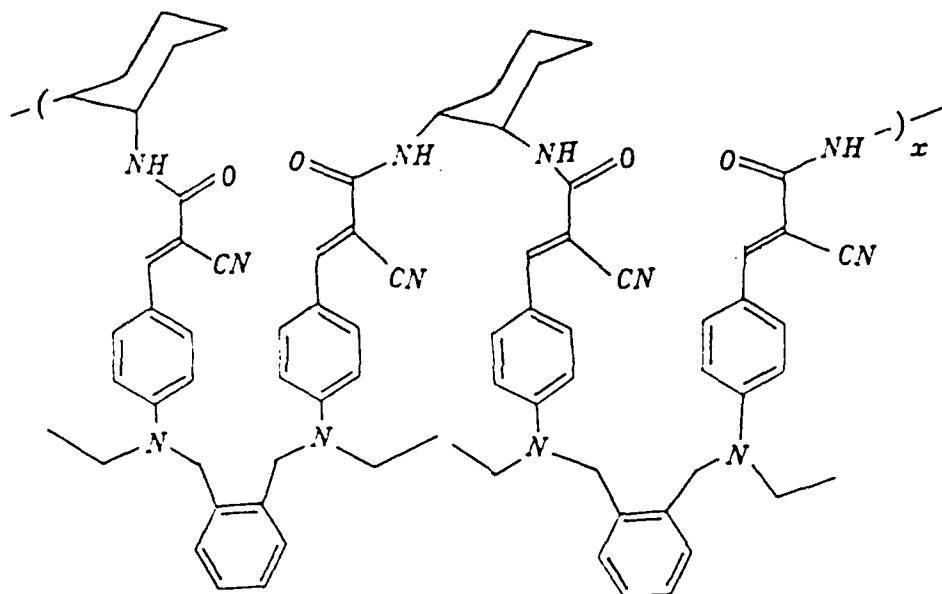
The behavior of the polar orientational order parameter of two nonlinear optical (NLO) polymers is investigated using the second harmonic generation (SHG) and the refractive index/waveguide apparatus. The two NLO systems consist of a MNA/PMMA guest/host and a BCSC according main chain polymer. (See text for the exact names of acrolyms.) The MNA/PMMA results show the inadequacy of the independent dipole orientation model for the description of the electric field poling. The BCSC system illustrates the birefringence in the refractive index is not a necessary criterion for the second order nonlinear effect such as SHG.

1. INTRODUCTION

Organic molecules, with a conjugated π -electron system terminated by donor and acceptor groups, are known to exhibit a large second order hyperpolarizability.¹ Polymer systems containing these molecules can be made to produce a large second order nonlinear optical (NLO) effect, such as the second harmonic generation. To obtain an active NLO polymeric material, in addition to selecting chromophores with large second order hyperpolarizability β to incorporate them into polymer chains, polar orientational order for the chromophores must be induced. The most common method employed to impart polar orientational order in the polymer system is by electric field poling.² This is carried out by processing the polymer containing NLO chromophores as a film. The polymer film is heated above its glass transition temperature (T_g) in the presence of a strong electric field ($> 10^4$ V/cm); the film is then cooled down below T_g to lock the chromophore orientation in place before the field is removed. The poling process breaks down the isotropic symmetry of the amorphous polymer film and freezes the NLO chromophores in the noncentrosymmetric order.²

Thus, to process polymeric NLO materials in order to exhibit large second order optical effects, the most fundamental quantity is the polar orientational order parameter (POP). Other types of orientational order that are not polar are not essential to the second order NLO effect. When the POP vanishes, the second order NLO also vanishes. To maximize the NLO effect, it is thus important to understand the behavior of POP connected with the poling process. The dependence of the NLO chromophore concentration of POP is also important.

In this paper we report results of studies of two types of NLO polymers to show the specific behavior of POP. One deals with a guest/host polymer: 2-methyl 4-nitroaniline/poly(methyl methacrylate) or MNA/PMMA, and the other with a main chain accordion polymer, 1,2-benzyl-1,2-cyclohexyl-bridged syndioregic α -cyano cinnamamide (BCSC), whose chemical formula is given by



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In the MNA/PMMA system, the concentration dependence of the second order susceptibility, $\chi(2)$ ($-2\omega; \omega, \omega$) is obtained from fitting a theoretical expression to the measured intensities of second harmonic generation (SHG) at different polarizations. We use the BCSC system to show that nonpolar orientational order does not contribute to SHG; it is the polar order that is essential for SHG.

2. EXPERIMENTAL

For the MNA/PMMA systems, appropriate amounts of MNA and PMMA were dissolved in chloroform to form solutions of various chromophore concentration. The amount of chloroform in each solution was adjusted to give rise to a desired viscosity suitable for spin coating. The solutions were filtered to remove undissolved particulates. Films were prepared by spin coating the polymer solution on the soda lime glass slides, which were pre-coated with 300Å SiO_2 and 250Å ITO. A similar ITO coated soda lime glass slide was then placed on top of the polymer/ITO glass slide to form a sandwich configuration for electrode poling. The NLO polymer/ITO sample assembly was placed in a vacuum oven at 25°C for more than 24 hours in order to remove the solvent used in spin coating.

The BCSC polymer was provided by Dr. Geoffrey Lindsay's research group at the Naval Weapon Laboratory, China Lake, CA. To prepare the BCSC polymer films for the optical measurements, the polymer was first dissolved in chloroform, after ultracentrifugation to remove the undissolved particulate, the polymer solutions was spin coated on a ITO substrate or a fused quartz wafer under dry nitrogen environment to avoid contamination by the atmospheric humidity. After spin coating, the films were kept in a vacuum oven at 200°C for 24 hours for annealing and also for removing the solvent before heating it to 215°C for poling under corona discharge.

The glass transition temperatures of the samples were determined by a DSC (Perkin Elmer Delta series). The glass transition temperature of BCSC is 193°C, and that of the MNA/PMMA system varies with the MNA concentration. The refractive indices of the samples were determined by a prism

coupler (Matricon) modified for the multiple wavelength operation. The prism coupler is operated in accordance with the optical waveguide principle with the polymer film served as the propagation layer in the slab waveguide configuration. Absorption spectra were recorded with an HP 8452A diode array UV-VIS spectrometer. The intensity of the absorption spectrum was used to calibrate the chromophore concentration of the sample.

The second harmonic generation (SHG) experimental setup is shown in Fig. 1.

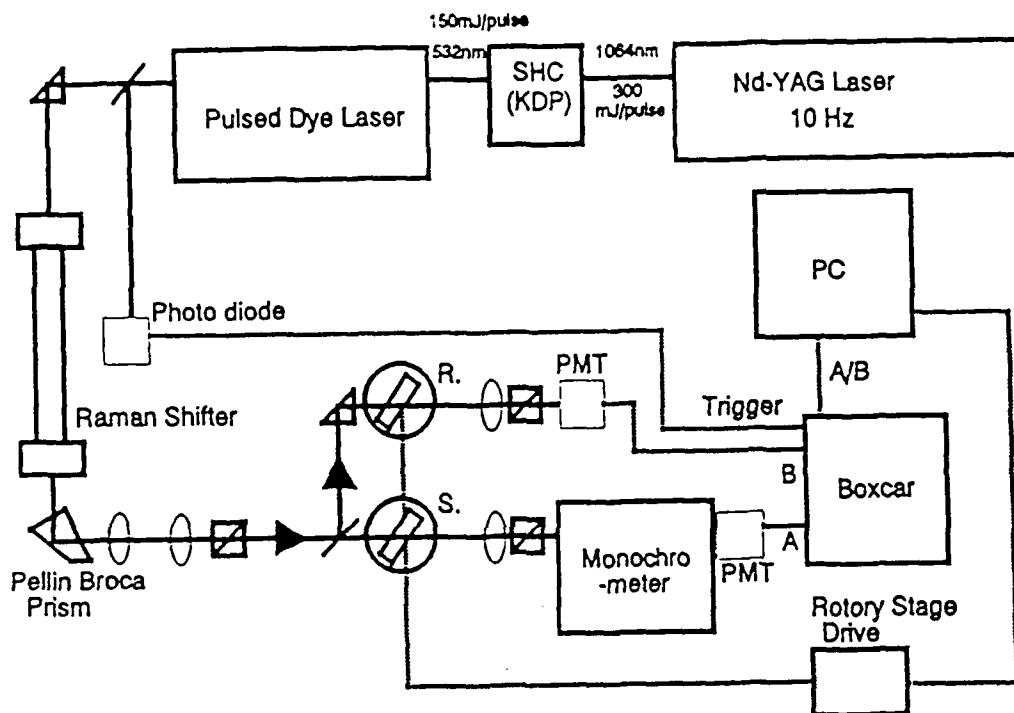


Fig. 1 The second harmonic generation experimental set up. Symbols R and S refer to reference and sample, respectively. PC is personal computer and PMT is photomultiplier tube. SHC is second harmonic crystal. The other notations are self-explanatory.

A Nd:YAG laser (Spectra-Physics GCR-11, $\lambda = 1.06 \mu\text{m}$, Q-switched at 10 Hz, 250 mJ per pulse) was used to measure the second order nonlinear susceptibility of the poled NLO polymer film, which was mounted on a computer controlled goniometer stage. The film mounted on the ITO electrodes was heated in a heating/cooling device on the goniometer stage. For the MNA/PMMA film, the electrode or corona poling was employed simultaneously during the optical measurement. The fundamental wave was blocked by a short-pass filter. The second harmonic signal, obtained in transmission, was selected from a monochromator. It was detected by a photomultiplier tube, followed by a pre-amplifier, and finally averaged by a boxcar integrator (EG & G 4422). The boxcar output was interfaced to a PC. The Maker fringes of a single crystal quartz plate ($d_{11} = 0.5 \text{ pm/V}$) were used as reference to determine the incident laser power employed in the measurement of the second order susceptibilities of the samples.

3. RESULTS AND DISCUSSION

Shown in Fig. 2 are the boxcar outputs of the SHG signals plotted versus the goniometer rotation angle ϕ for the MNA/PMMA films at different MNA concentrations obtained with the incident beam in the p polarization. Here ϕ is the angle between the propagation direction and the normal to the film surface.

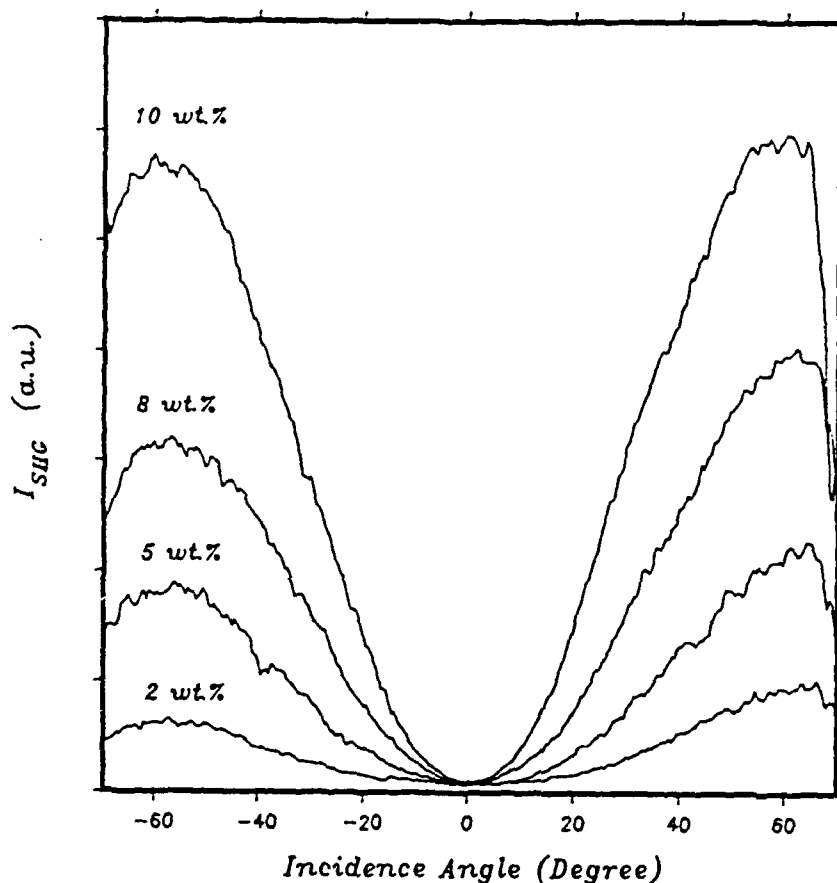


Fig. 2 The SHG signals of the MNA/PMMA films at different MNA concentrations obtained with the incident beams in the p polarization plotted versus the goniometer rotation angle ϕ .

In Fig. 3 is shown the refractive index dispersion obtained for the BCSC film before and after poling for light polarized in p and s polarizations. One note a large difference in the two refractive indices at different polarizations before the film is poled, thereby indicating that a significant ordering of the BCSC polymer on the fused quartz wafer after spin coating which cannot be removed by annealing. Since the refractive index of the light at the S-polarization (TE) is higher than that at the p polarization (TM), parts of the BCSC polymer chain lie on the surface of the substrate. After the poling the refractive index for the s polarization decreases slightly, whereas that for the p polarization increases significantly; the two refractive indices become quite similar. Thus, after poling the orientation of the polar group lies in the direction perpendicular to the substrate. This result is probably one of the first example to show that the refractive index difference for the TE and TM

modes is not a necessary criterion for indicating polar order. A sample with non-polar order always shows a birefringence, whereas the polar order does not necessarily show a birefringence in the refractive index.

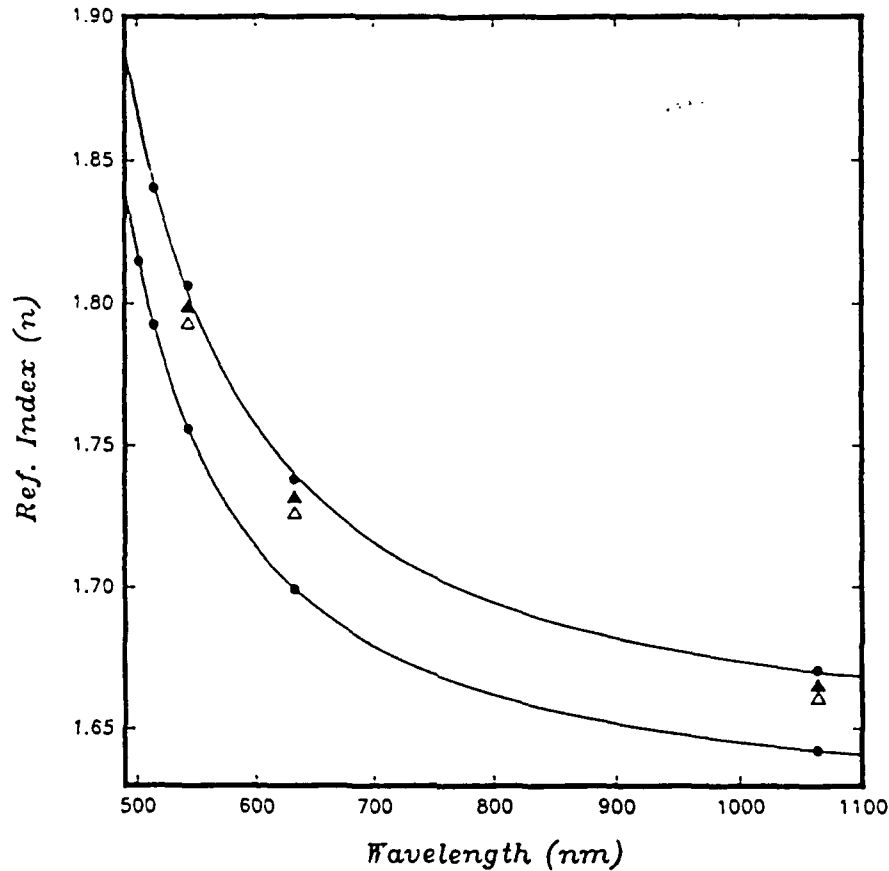


Fig. 3 The refractive index dispersion for the BCSC film before and after poling. ▲, an ▼ for TE and TM after poling, respectively. Dots guided by lines are results before poling.

While there is a large birefringence in the unpoled sample, no SHG intensity was detected. On the other hand, after corona poling, a large SHG intensity emits from the BCSC film. Shown in Fig. 4 are the SHG signals detected in transmission for the poled BCSC film (1 μm thickness) at room temperature excited by the 1.06 μm fundamental beam in p and s polarizations, together the crystalline quartz (2 mm thickness) reference.

For an isotropic film subject to a poling electric field in the direction perpendicular to the film surface, the transmitted second harmonic power density $I_{2\omega}$ for a material with a nonlinear optical coefficient $d = \frac{1}{2} \chi^{(2)}$ ($-2\omega; \omega, \omega$) is given by ³

$$I_{2\omega} = \frac{(8\pi)^3}{c} I_{\omega}^2 P^2(\phi) d^2 \left[\frac{T_{2\omega}(\phi)}{(n_{\omega}^2 - n_{2\omega}^2)^2} \right] \sin^2 \left(\frac{\pi \ell}{2\ell_c} \right) \quad (1)$$

where c is the velocity of light in vacuum; I_{ω} is the power density of the fundamental beam inside

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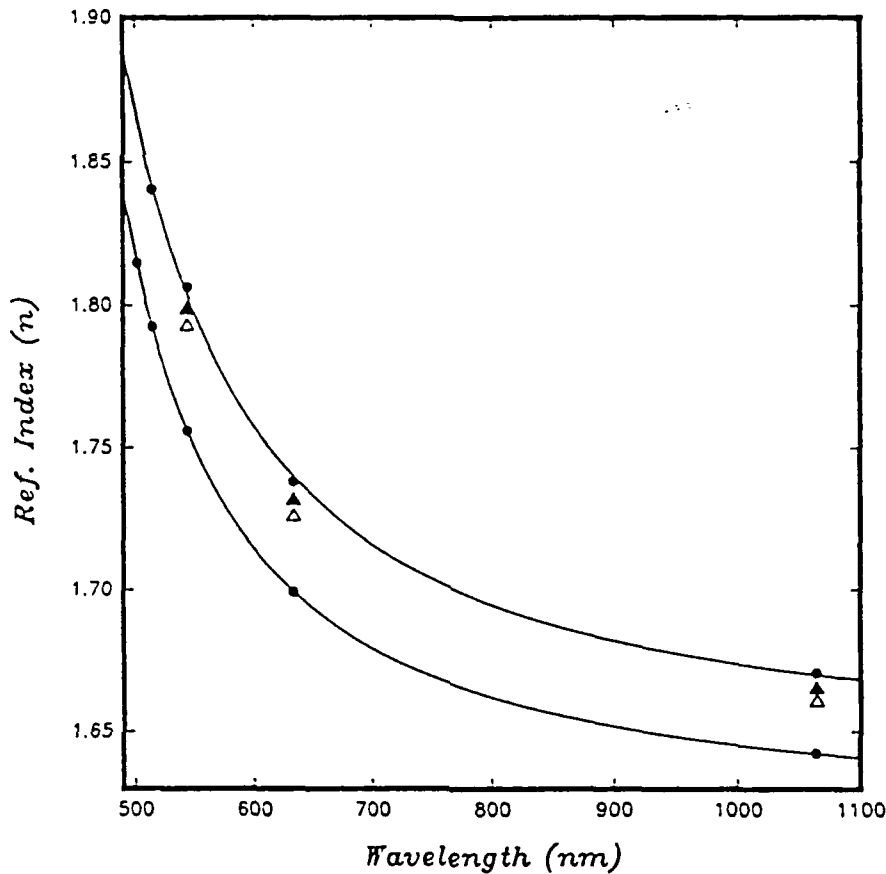


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where c is the velocity of light in vacuum; I_{ω} is the power density of the fundamental beam inside

the medium; $P(\phi)$ is the projection factor. $T_{2\omega}(\phi)$ is the transmission factor. Both $P(\phi)$ and $T_{2\omega}$ depends on the polarization of the incident beam, the incidence angle, as well as the refractive index of the material at fundamental (n_ω) and at second harmonic ($n_{2\omega}$) frequencies. The quantity ℓ_c is the correlation length; it is given by: $\ell_c = \lambda/4(n_\omega \cos \phi'_\omega - n_{2\omega} \cos \phi'_{2\omega})$, where ϕ'_ω and $\phi'_{2\omega}$ are the angles of refraction of the fundamental and the second harmonic beams, respectively. They are related to the incident angle ϕ by Snell's law as: $\sin \phi'_\omega = \sin \phi/n_\omega$ and $\sin \phi'_{2\omega} = \sin \phi/n_{2\omega}$. We obtained the nonlinear optical coefficients by fitting the measured intensities in both the p and s polarizations versus angle (ϕ) data to Eq. (1). We used the Maker fringes of the quartz plate to determine the incident intensity of the fundamental beam needed in Eq. (1). Other data needed for the fit were the film thickness ℓ and the refractive indices n_ω and $n_{2\omega}$ were determined by waveguide experiments involving the use of a prism coupler. The steady state value of $\chi_{31}^{(2)}$ at 532 nm in the MNA/PMMA systems at 90°C plotted as a function of MNA concentration in Fig. 5.

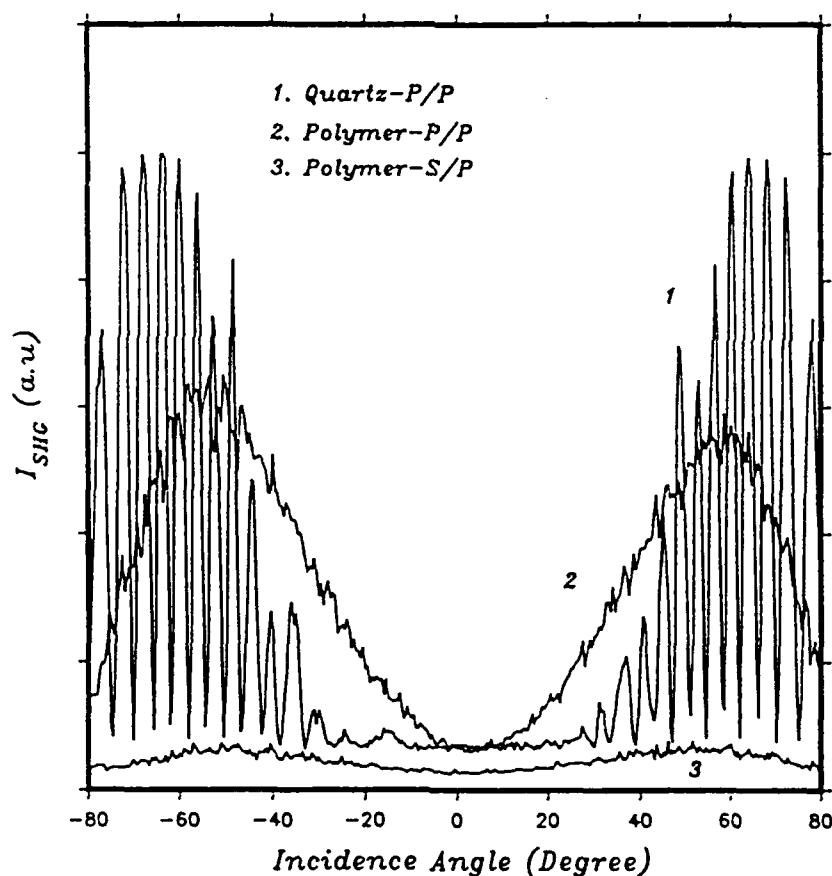


Fig. 4 The SHG signals of the poled BCSC film (1 μm thickness) at room temperature excited by 1.06 μm fundamental beam in the p and s polarizations. The Maker fringes of crystalline quartz is shown as a reference. Notation p/p p/s indicates incident polarization is p and detected polarizations are p and s, respectively.

The $\chi_{31}^{(2)}$ and $\chi_{33}^{(2)}$ values at 532 nm for the BCSC accordion at room temperature are 1.90 pm/v and 7.08 pm/v. Those values are stable for over weeks without decay. A complete stability study of the $\chi^{(2)}$ values at elevated temperatures is in progress and will be reported elsewhere. Note the

$\chi_{33}^{(2)}/\chi_{31}^{(2)}$ ratio is 3.73, greater than the predicted weak field value.⁶ The second order susceptibilities are related to the polar orientational order (POP) parameters by^{1,2}

$$\chi_{33}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 \langle \cos^3 \theta_1 \rangle \quad (2)$$

and

$$\chi_{31}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 (\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle)/2 \quad (3)$$

where ρ is the number density of the chromophores and β is the dominant component of the hyperpolarizability tensor along the molecular principal axis. The subscript 1, associated with θ_1 , refers to the representative NLO chromophore 1. In the Lorentz model, the local field factors $f_{2\omega}$ and f_{ω} are given by $f_{2\omega} = (n_{2\omega}^2 + 2)/3$ and $f_{\omega} = (n_{\omega}^2 + 2)/3$, respectively. The POP for $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$ are thus $L_{33} = \langle \cos^3 \theta_1 \rangle$, and $L_{31} = 1/2 [\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle]$, respectively. Here the angular brackets denote the ensemble average in the presence of the poling field. Both L_{33} and L_{31} are functions of the poling parameter a .

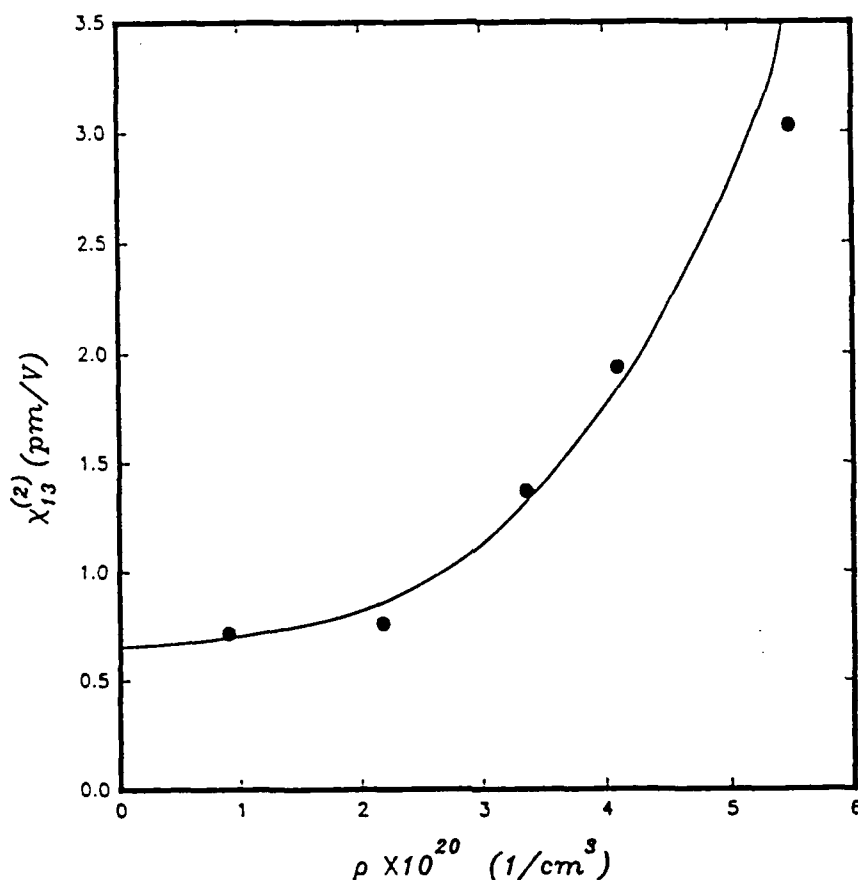


Fig. 5 The steady state value of $\chi_{31}^{(2)}$ at 90°C for the MNA/PMMA system plotted as a function of MNA concentration. The usual theoretical description of the POP owing to electric field poling is based on the independent dipole orientation model.² In this model, the POPs are simply given by the Langevin function of order n , $L_n(a)$, where $a = f_0 \mu E_p / kT$, f_0 is the local field factor associated with the poling field E_p , μ is the dipole moment of the NLO chromophore. One consequence of the independent dipole orientation approach is that the POP associated with the second order macroscopic susceptibility is practically independent of the concentration of the NLO chromophores.

This result is not in agreement with the electro-optical measurement,⁴ and the SHG result in guest host system, as shown in Fig. 5. The POP calculated from $\chi^{(2)}$ will show a concentration dependence, which is not in agreement with the independent dipole orientation model. A recent calculation, based on a statistical mechanics approach, has shown that the POP is in general a complex function of the chromophore concentration ρ .⁵ In the specific case of the dipole-dipole interaction mechanism, the complex concentration dependence of the POP can be expressed in terms of the Kirkwood g-factor associated with the orientational pair correlation of the interacting dipoles, which is, in turn, related to the dielectric constant of the medium.⁶ A more complete study of the effect of orientational pair correlation on POP in the weak and strong poling field conditions is presented in more detail elsewhere.⁷

In conclusion, we have investigated the behavior of the polar orientational order parameter using SHG and refractive index birefringence. We have obtained $\chi^{(2)}$ as a function of concentration for the MNA/PMMA system to show the concentration dependence of POP. We have shown that the usual independent dipole orientation model is inadequate to the description of the experimental result. In the BCSC accordion NLO polymer system, we have shown that birefringence in the refractive index is not a criterion for the 2nd order effect; rather, polar orientation order essential to SHG may not give rise to a birefringence in the refractive index.

4. ACKNOWLEDGEMENT

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